

DE 101 58 233 A1

Specification

[0001] The present invention relates to a reactive system for 3D printing, comprising at least one first component and at least one second component, the first and second components reacting chemically with one another after the addition of a liquid medium and forming a solid with improved physical properties, preferably improved mechanical properties and/or water resistance.

[0002] In 3D printing a powder such as a ceramic, metal or bulk polymer powder is applied in layers on top of each other and smoothed in each case using a roller or miller. Following each layer application the powder is printed by means of an ink using the ink-jet process. The ink leads to solidification of the powder in the layer and between the layers.

[0003] Following the printing process and a certain drying time, the 3D object is taken out of the powder bed and released from loose, unbonded powder. The powder which has not solidified can be used again in the printing process. In the case of water-soluble polymers, the 3D object must subsequently be chemically modified by post-treatment and made water-insoluble.

[0004] In 3D printing a binder is available according to the powder used either in the ink or in the powder material.

[0005] In US-PS 5,204,055 a 3D printing technique is described in which a ceramic, metal or plastic powder (e.g. aluminium oxide, zirconium oxide) is bonded with a dissolved, liquid or colloidal binder which is distributed as an ink with a print head. The binder penetrates the porous powder layer and thereby combines the powder particles with each other in and between the layers. The binder may be organic or inorganic.

[0006] The organic binders described in US-PS 5,204,055 are either water-soluble materials (cellulose binders) polymer resins soluble in volatile organic solvents (butyral resins) or ceramic precursors (polycarbosilazane). Inorganic binders described in US-PS 5,204,055 comprise e.g. tetraethyl orthosilicate.

[0007] The objects obtained by 3D printing are, according to US-PS 5,204,055, usually subjected to a further post-treatment such as burning whereby the binder is either removed or additional solidification by sintering takes place. The disadvantage of the 3D technique, described in this patent, lies in the fact that blockage of the jets often occurs on account of the binder and particularly when high dispersion concentrations are used.

[0008] If the binder is situated in the powder, a solvent is sprayed by the print head which initially dissolves the binder and thus causes bonding of neighbouring powder particles. The curing process finally takes place physically through the volatilisation of the solvent.

[0009] In the case of the inks used here a difference is made between water-containing and non-water-containing inks. In the case of the non-water-containing inks chloroform has been used in a modified 3D printing process for bonding a polymer powder (polyactide) consisting of only one component (R.A. Giordano et al., J. Biomater. Sci. Polymer Edn., 1996, 8, 63-75). The 3D objects obtained here are distinguished by water insolubility. Owing to the toxicity of the chlorinated organic solvent used, this process, however, is not suitable for use in an office environment and is only sensible for special applications. The print heads used in this process are also considerably more expensive than print heads for aqueous inks.

[0010] The toxicologically more advantageous aqueous systems dissolve a binder contained in the powder which bonds the powders through subsequent drying (US-PS 5,902,441). According to US-PS 5,902,441 the ink can contain, in addition to water, process aids such as humectants (preferably glycerine), flow rate accelerators (e.g. ethylene glycol diacetate, isopropanol) and colour. The binders are water-soluble polymers, carbohydrates, sugars, sugar derivatives, proteins and various inorganic compounds. If plaster of paris is used as an inorganic powder, a solidification of the powder to form the 3D object occurs through water-induced changes in the crystals by means of incorporation of water of crystallisation.

[0011] In order to improve the mechanical properties of the component, fillers (starch, e.g. maltodextrin) and fibres (e.g. cellulose fibres, graphite fibres, glass fibres), in addition to the binder, are, according to US-PS 5,902,441, mixed with the powder, coating of the filler with the binder is also possible. Fibre and filler are either insoluble in the ink or dissolve much more slowly than the binder component. If necessary, another printing aid (e.g. lecithin, polypropylene glycol) can also be added. This provides, before the printing process, a weak adhesion between the powder particles and thereby reduces dust formation as well as distortion within the printed layers. A typical composition for such a powder according to US-PS 5,902, 441 can be seen in the following Table 1:

Table 1

Powder component	Material used	Composition (weight by %)	Particle size (μm)
Binder	Saccharose	30	10
Reinforcing fibre	Cellulose	10	100
Filler	Maltodextrin	48.5	< 300
Stabilising fibre	Cellulose	10	60
Printing aid	Lecithin	1.5	-

[0012] After cleaning the object obtained, it can again be subjected to various post-treatment steps. Heat treatment and wax or resin infiltration increase the mechanical strength of the object. Infiltration reduces the porosity and makes the object water-resistant. In addition, coating and sanding are also possible.

[0013] In systems to date, in which the binder is situated in the powder and only a solvent is added via the print head, the unbinding process takes place either during the evaporation of an organic solvent (polylactide system) or of water (water-soluble polymers, carbohydrates, sugar, sugar derivatives, proteins) or by the incorporation of water of crystallisation (plaster of paris), and not by a purely chemical reaction (reactive bonding).

[0014] In the case of known 3D objects, therefore, the basic problems arises that they disintegrated through contact with water into their original powder components. In the case of the plaster of paris system also used, one obtains no water-resistant objects as the water quantity used in the process is too small to bring about complete crystallisation. If unbound plaster of paris is brought into contact with water subsequently, a jump in expansion (hygroscopic expansion) takes place which results in a distortion of the 3D object.

[0015] The mechanical properties of the known 3D objects are not good enough and frequently necessitate subsequent infiltration.

[0016] It is, therefore, the object of the present invention to create a reactive system which produces 3D objects with improved physical properties like improved mechanical properties and/or water resistance after the printing process with a liquid medium on the basis of a chemical reaction between the components of the reactive system has taken place.

[0017] This object is achieved by the reactive system according to patent claim 1 of the present invention.

[0018] The reactive system according to the invention is explained in detail below.

[0019] Advantages compared to the systems to date are, for example, improved mechanical strength and/or water resistance with only slight shrinkage of the 3D object obtained.

[0020] Fig. 1 shows a test specimen which has been produced from a reactive system according to the invention and as comparison examples of test specimens which have been produced from known powder systems for 3D printing.

[0021] In its general embodiment the reactive system of the present invention comprises at least one first component and at least one second component. The first and the second components are reacting chemically with one another after addition of a liquid medium which acts as a solvent or swelling agent. The chemical reaction is used for the reactive bonding of the individual components of the reactive system within the layer and between the layers.

[0022] In a more special embodiment of the reactive system of the present invention, the reactive system comprises at least one polyelectrolyte and at least one further reactive component which is at least one further polyelectrolyte or at least one inorganic reactive component.

[0023] The reactive bonding is based in this embodiment on the complexing of a polyelectrolyte by one or more of the further reactive components named above.

[0024] In the case of the polyelectrolytes it is a matter of either a polyacid (e.g. polyacrylic acid), a polybase (e.g. polyvinyl pyridine), a polyanion (e.g. sodium salt of polyacrylic acid) or a polycation (e.g. polyvinyl pyridine hydrochloride).

[0025] Six types of polyelectrolyte reactive systems as embodiments of the present invention will be described below.

Reactive system I

Reaction of one/more polyacid(s) with one/more polybase(s)

[0026] This system consists of at least one polyacid as well as at least one polybase which are easily soluble or swellable (in the case of fillers which are grafted with polyelectrolytes) in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water and are only slightly hydroscopic and in the dissolved state reveal only small viscosity.

[0027] The ink from the printing jet dissolves the polyelectrolytes and distributes them quickly within the powder bed. As soon as a dissolved or swollen polyacid comes into contact with a dissolved or swollen polybase, a chemical

reaction occurs and thus the formation of a preferably water-resistant polyelectrolyte-polyelectrolyte complex. Curing and thus reactive bonding within the layer and between the layers is the consequence.

[0028] Average particle sizes for the polyelectrolytes lie below 300 μm . Typical average particle sizes for the polyelectrolytes lie between 1 and 300 μm , between 20 and 150 μm , more preferably between 30 and 100 μm and in particular between 30 and 80 μm .

[0029] The reactive components can, in addition to the unimodal grain size distribution, reveal a polymodal (bimodal, trimodal) grain size distribution. The distribution is preferably chosen so that the powder particles achieve the highest possible packing density.

[0030] Suitable polyacids/bases are biopolymers, chemically modified biopolymers and synthetic polyacids/bases. Non-restrictive examples of these polyelectrolytes are indicated below:

Polyacids

[0031] Alginic acid, gum arabic, nucleic acids, pectins, proteins (biopolymers), carboxymethylcellulose, ligninsulphonic acids, acid-modified starch (chemically modified biopolymers), polymethacrylic acid, polymethacrylic acid copolymer with methyl methacrylate, polyvinyl sulphonic acid, polystyrene sulphonic acid, polysulphuric acid, polyvinyl phosphonic acid, polyvinyl phosphoric acid, the homo- and copolymers of unsaturated aliphatic carbonic acids such as acrylic acid, itaconic acid, mesaconic acid, citraconic acid, aconitic acid, maleic acid, fumaric acid, glutaconic acid, tiglic acid and methacrylic acid and the anhydrides of these carbonic acids (e.g. itaconic acid anhydride). These polycarbonic acid anhydrides form precursors of the polycarbonic acids which are transferred by water contact into polycarbonic acid. Further suitable polyacids are the copolymers of the polyacids with acrylic amide, acrylic nitrile, acrylic acid esters, vinyl chloride, allyl chloride, vinyl acetate and 2-hydroxyethyl methacrylate (synthetic polyelectrolytes).

Polybases

[0032] Chitosan (chemically modified biopolymer), polyethylenimine, linear and cross-linked polyallylamine, polyvinylamine, polyvinylpyridine, polydiallyl dimethylamine, poly[2-(N,N-dimethylamine)-ethylacrylate], poly[4-(N,N-dimethylamine)methylstyrene] and the copolymers of the polybases with acrylamide, acrylic nitrile and acrylic acid esters (synthetic polyelectrolytes).

[0033] It is not absolutely essential that polyacid and polybase are present in two different powder components. Copolymers made of polyacid and polybase may also be used [e.g. poly-(acrylic acid-co-vinylpyridine)] in which both reactive groups (acid and base group) are present in one polyelectrolyte.

[0034] Typical stoichiometric ratios of the reactive groups of the polyelectrolytes (e.g. $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{NH}_2$) to each other are indicated in the following Table 2, $n(\text{SH})$ and $n(\text{B})$ being calculated according to the following formula:

$$n(\text{SH}) = \frac{n(\text{SH})}{n(\text{SH}) + n(\text{B})} * 100\% \quad ; \quad n(\text{B}) = \frac{n(\text{B})}{n(\text{SH}) + n(\text{B})} * 100\%$$

Table 2

Stoichiometric ratios of the reactive groups	Typical	Preferred	In particular
$n(\text{SH})$ polyacid	20-80 %	40-60 %	~ 50 %
$n(\text{B})$ polybase	80-20 %	60-40 %	~ 50 %

Reactive system 2

Reaction of one/more polyanion(s) with one/more polycation(s)

[0035] This system consists of at least one polyanion as well as at least one polycation which are easily soluble or swellable in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water and are only slightly hygroscopic and in the dissolved state reveal only small viscosity.

[0036] The ink from the printing jet dissolves the polyelectrolytes and distributes them quickly within the powder bed. As soon as a dissolved or swollen polyanion comes into contact with a dissolved or swollen polycation, a chemical reaction occurs and thus the formation of a preferably water-resistant polyelectrolyte-polyelectrolyte complex. Curing and thus reactive bonding within the layer and between the layers is the consequence.

[0037] The typical particle sizes for the polyelectrolytes correspond to the particle sizes stated for the polyelectrolytes of reactive system 1. The reactive components, in addition to the unimodal grain size distribution, reveal a polymodal (bimodal, trimodal) grain size distribution. The distribution is preferably chosen so that the powder particles achieve the highest possible packing density.

[0038] Suitable polyanions/polycations are biopolymers, chemically modified biopolymers and the salts of synthetic polyacids/bases. Non-restrictive examples of these polyelectrolytes are indicated below:

Polyanions

[0039] The sodium, ammonium or potassium salts of the above-stated polyacids (partly or fully neutralised).

Polycations

[0040] The ammonium compounds or the quaternary ammonium compounds (as chlorides) of the above-stated polybases (partly or fully neutralised).

[0041] Typical stoichiometric ratios of the reactive groups of the polyelectrolytes (e.g. $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{NH}_3^+$) to each other are indicated in the following Table 3, $n(\text{S}^-)$ and $n(\text{B}^+)$ being calculated according to the following formula:

$$n(\text{S}^-) = \frac{n(\text{S}^-)}{n(\text{S}^-) + n(\text{B}^+)} * 100\% \quad ; \quad n(\text{B}^+) = \frac{n(\text{B}^+)}{n(\text{S}^-) + n(\text{B}^+)} * 100\%$$

Table 3

Stoichiometric ratios of the reactive groups	Typical	Preferred	In particular
$n(\text{S}^-)$ polyacid	20-80 %	40-60 %	~ 50 %
$n(\text{B}^+)$ polybase	80-20 %	60-40 %	~ 50 %

Reactive system 3

Reaction of one/more polyacid (s) with one/more inorganic reactive component(s)

[0042] The system consists of at least one polyacid which is easily soluble or swellable in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water and is only slightly hygroscopic and in the dissolved state reveals only small viscosity and of at least one inorganic reactive component which is either soluble or insoluble or only slightly hygroscopic in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water.

[0043] The water-containing ink from the printing jet dissolves the water-soluble reactive components and distributes them quickly within the powder bed. As soon as a dissolved or swollen polyacid comes into contact with the inorganic reactive component, the polyacid reacts with the acid-active inorganic reactive component with neutralisation into a preferably water-resistant polyelectrolyte complex. Curing and thus reactive bonding within the layer and between the layers is the consequence.

[0044] Typical particle sizes for the polyelectrolytes correspond to the particle sizes indicated for reactive system 1. Typical particle sizes for the inorganic reactive components lie below 300 μm . Typical average particle sizes for the inorganic reactive components lie between 1 and 300 μm , between 5 and 150 μm , more preferably between 20 and 100 μm and in particular between 20 and 80 μm . Broad grain size distributions are preferred. It is preferred for the water resistance of the 3D objects if a fine portion of at least 10 % by volume lies below 10 μm . However, the fine portion should not be chosen too high as problems can occur with the layer application, the distribution of the liquid medium in the layer and excessive dust development. As the liquid medium is applied by the inkjet print heads at a certain pressure, the risk of "layer destruction" exists with too high a fine portion, as fine powder is "blown away". The reactive components can, in addition to the unimodal grain size distribution, also reveal a polymodal (bimodal, trimodal) grain size distribution. The distribution is preferably chosen so that the powder particles achieve the highest possible packing density.

[0045] Suitable inorganic reactive components are weakly hygroscopic calcium, aluminium and zinc salts. In addition, such compounds are suitable as inorganic reactive components which are normally used in the dental branch with ionomers to form ionomer cements like metal oxides, e.g. zinc oxide, the sinter ceramics thereof and ion-releasing glasses as described, for example, in the US patents 3,655,605, 3,814,717, 4,143,018, 4,209,434, 4,360,605 and 4,376,835.

[0046] Preferred inorganic reactive components are acid-reactive components. Preferred metal oxides comprise titanium dioxide, zirconium oxide, aluminium oxide (neutral, acidic, basic), barium oxide, calcium oxide, magnesium oxide, zinc oxide as well as the sinter ceramics thereof such as zinc oxide/magnesium oxide. Preferred metal salts comprise, for example, aluminium chloride, aluminium stearate, aluminium sulphate, aluminium acetate, aluminium nitrate, calcium carbonate, calcium ascorbate, calcium stearate, calcium lactate, calcium saccharate, calcium hydrogen phosphate, calcium chloride, calcium hydroxide, calcium phosphate, calcium acetate, hydroxylapatite, calcium nitrate, calcium fluoroborate, zinc chloride, zinc stearate, zinc acetate, zinc gluconate, zinc sulphate, barium nitrate, strontium nitrate, the hydroxides of magnesium, calcium, barium, aluminium, boron, zirconium, hafnium, titanium, chromium, vanadium and the oxide hydroxides of aluminium, zirconium, hafnium, titanium, chromium and vanadium. Preferred ion-releasing glasses comprise borate glasses, phosphate glasses, fluoroaluminium silicate glasses and calcium aluminium silicate glasses. Mixtures of the inorganic reactive components may also be used.

[0047] Zinc oxide/magnesium oxide sinter ceramics and calcium aluminium silicate glasses are particularly preferred.

[0048] Suitable polyacids are the above-mentioned ones. Preferred polyacids are the homo- and copolymers of polyacrylic acid.

[0049] Typical mass ratios of the polyacid(s) and the inorganic compound(s) to each other are indicated in Table 4 below:

Table 4

Mass ratio	Typical	Preferred	In particular
Polyacid	> 2 %	5-75 %	5-25 %
Inorganic compound with multivalent cation	< 98 %	25-95 %	75-95 %

Reactive system 4

Reaction of one/more polyanion(s) with one/more inorganic reactive component(s)

[0050] The system consists of at least one polyanion which is very easily soluble or swellable in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water and is only slightly hygroscopic and in the dissolved state reveals only small viscosity and of at least one inorganic reactive component which in an ink which comprises water, aqueous-organic or organic solvents miscible with water is either soluble or insoluble and only slightly hygroscopic.

[0051] The water-containing ink from the printing jet dissolves the water-soluble reactive components and distributes them quickly within the powder bed. As soon as a dissolved or swollen polyanion comes into contact with the inorganic reactive component, the polyanion reacts with the inorganic reactive component with neutralisation and/or salt formation into a preferably water-resistant polyelectrolyte complex. Curing and thus reactive bonding within the layer and between the layers is the consequence.

[0052] Typical particle sizes for the polyelectrolytes and for the inorganic reactive components correspond to the particle sizes indicated for reactive system 3. The reactive components, in addition to the unimodal grain size distribution, can also reveal a polymodal (bimodal, trimodal) grain size distribution. The distribution is preferably chosen so that the powder particles achieve the highest possible packing density.

[0053] Suitable polyanions are the anions of the polyacids already mentioned above (partly or fully neutralised). Preferred polyanions are the anions of the homo- and copolymers of polyacrylic acid. Suitable inorganic reactive components are those which have been stated for reactive system 3.

[0054] Typical mass ratios of the polyanion(s) and the inorganic compound(s) to each other are indicated in Table 5 below:

Table 5

Mass ratio	Typical	Preferred	In particular
Polyacid	> 2 %	5-75 %	5-25 %
Inorganic compound with multivalent cation	< 98 %	25-95 %	75-95 %

Reactive system 5

Reaction of one/more polybase(s) with one/more inorganic reactive component(s)

[0055] The system consists of at least one polybase which is very easily soluble or swellable in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water and is only slightly hygroscopic and in the dissolved state reveals only small viscosity and of at least one inorganic reactive component which is either soluble or insoluble or only slightly hygroscopic in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water.

[0056] The water-containing ink from the printing jet dissolves the water-soluble reactive components and distributes them quickly within the powder bed. As soon as a dissolved or swollen polybase comes into contact with the inorganic reactive component, the polybase reacts with the inorganic reactive component with neutralisation into a preferably water-resistant polyelectrolyte complex. Curing and thus reactive bonding within the layer and between the layers is the consequence.

[0057] Typical particle sizes for the polyelectrolytes and for the inorganic reactive components correspond to the particle sizes indicated for reactive system 3. The reactive components can, in addition to the unimodal grain size distribution, also reveal a polymodal (bimodal, trimodal) grain size distribution. The distribution is preferably chosen so that the powder particles achieve the highest possible packing density.

[0058] Suitable polybases are the polybases mentioned above. Suitable reactive components are slightly hygroscopic phosphates, hydrogen phosphates, diphosphates, triphosphates, sulphates, sulphites, disulphates, thiosulphates, tetraborates and water-soluble sodium, potassium and ammonium salts thereof.

[0059] Typical mass ratios of the polybase(s) and the inorganic compound(s) to each other are indicated in Table 6 below:

Table 6

Mass ratio	Typical	Preferred	In particular
Polybase	> 5 %	10-75 %	10-25 %
Inorganic compound with multivalent anion	< 95 %	25-90 %	75-90 %

Reactive system 6

Reaction of one/more polycation(s) with one/more inorganic reactive component(s)

[0060] The system consists of at least one polycation which is very easily soluble or swellable in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water and is only slightly hygroscopic and in the dissolved state reveals only small viscosity and of at least one inorganic reactive component which is either soluble or insoluble only slightly hygroscopic in an ink which comprises water, aqueous-organic solvents or organic solvents miscible with water.

[0061] The water-containing ink from the printing jet dissolves the water-soluble reactive components and distributes them quickly within the powder bed. As soon as a dissolved or swollen polycation comes into contact with the inorganic reactive component, the polycation reacts with the inorganic reactive component with neutralisation and/or salt formation into a preferably water-resistant polyelectrolyte complex. Curing and thus reactive bonding within the layer and between the layers is the consequence.

[0062] Typical particle sizes for the polyelectrolytes and for the inorganic reactive components correspond to the particle sizes indicated for reactive system 2. The reactive components can, in addition to the unimodal grain size distribution, also reveal a polymodal (bimodal, trimodal) grain size distribution. The distribution is preferably chosen so that the powder particles achieve the highest possible packing density.

[0063] Suitable polycations are the polycations stated above. Suitable inorganic reactive components are those which have been stated for reactive system 5.

[0064] Typical mass ratios of the polycation(s) and the inorganic compound(s) to each other are indicated in Table 7 below:

Table 7

Mass ratio	Typical	Preferred	In particular
Polycation	> 2 %	10-75 %	10-25 %
Inorganic compound with multivalent anion	< 95 %	25-90 %	75-90 %

[0065] Mixtures of the individual reactive systems may also be used.

[0066] It is not absolutely essential that each of the two/more reactive components of the reactive systems 1-6 are present as two different powder components before the printing process. They can either be mixed together dry beforehand or compounded to form a single powder component.

[0067] In addition, fillers and/or fibres can be coated before mixing with one or more polyelectrolytes or with the inorganic reactive component. The latter is used to increase the mechanical strength of the 3D objects. By coating inorganic-organic hybrid systems are obtained. If the polyelectrolytes are grafted on to the fillers and/or fibres, one obtains better adhesion between filler and polyelectrolyte. In these systems a covalent bond exists between the filler and the polybase/polycation or polyacid/polyanion. For grafting purposes, binders are used which are contained as comonomers in the polybase/polycation or polyacid/polyanion. A suitable binder is, for example, 3-(trimethoxysilyl)propyl methacrylate.

[0068] Typical average molecular weights of the polyelectrolytes in reactive systems 1 to 6 lie between 5000 and about 1,000,000 g/mol, more preferably between 5000 and about 250,000 g/mol and in particular between 5000 and about 100,000 g/mol. Mixtures of low and high molecular polyelectrolytes are also possible as these increase the flexibility of the 3D objects obtained.

[0069] If copolymers are used as polybases/polycations or polyacids/polyanions which have monomer units without reactive groups (e.g. acrylic amide), at least 10 % of the monomer units must consist of units with reactive groups.

[0070] If necessary, the inorganic reactive component used in reactive systems 3 to 6 may also be subjected to a surface treatment. Suitable surface treatments are, for example, washing with acid, treatment with reaction retarders such as tartaric acid, treatment with a silane or a silanol coupling agent. The latter is described, for example, in US PS 5,332,429 in connection with fluoroaluminium silicate glass.

[0071] Water-soluble reactive components may be contained in the powder and/or the ink.

Reaction retarder

[0072] As rapid surface reactions are usually involved in polyelectrolyte complexations, it is sometimes necessary to add a reaction retarder. The latter delays the curing reaction and thus facilitates better diffusion of the reaction partner in the dissolved polyelectrolyte. Thus one obtains a larger contact area between the reactants. Furthermore, the bonding of two layers to one another is also improved. The reaction retarders may in the reactive system be contained in the ink or both in the reactive system and in the ink.

[0073] Suitable anionic reaction retarders for inorganic polyelectrolyte complexes are substrates with a higher complex-formation constant to the multivalent cation than to the polyelectrolyte, e.g. salicylic acid, tartaric acid, dihydroxytartaric acid, oxalic acid, citric acid, ethylenediamine tetraacetic acid (EDTA) and their sodium and potassium salts, sodium phosphate, sodium dihydrogen phosphate as well as sodium hydrogen phosphate. Normally, the maximum proportion of chelating agents amounts to 20 % by weight referred to the polyacid. A preferred range lies between 0.01 and 10 % by weight.

[0074] Suitable cationic reaction retarders for polyelectrolyte complexes are substrates which release cations that do not form a solid with the polyacids, but only a gel such as magnesium oxide and tin fluoride. Normally, the proportion of the cationic reaction retarder amounts to less than 25 % by weight referred to the inorganic reactive components, a portion between 0.01 and 15 % by weight being preferred.

[0075] Typical average particle sizes for the reaction retarders lie between 1 and 100 μm .

Fillers/Fibres

[0076] In order to vary and improve the mechanical properties of the objects, the reaction system may also contain fillers and/or fibres. These can be added to the reactive system either dry or coated with one or more polyelectrolytes, inorganic reactive component(s) or reaction retarder(s). As described above, grafted fillers/fibres may also be used.

[0077] The fillers and fibres are either water-insoluble or only slightly soluble in water and wet very quickly. Suitable fillers and fibres comprise materials as already used for plastics. Examples of these are described in the "Handbook of Fillers" (G. Wypych "Handbook of Fillers", 2nd edition, ChemTec Publishing, Toronto, 1999).

[0078] For fillers it is preferred to use ceramics, glasses, naturally occurring materials and their synthetic derivatives and polymer fillers such as sand, quartz, silicon dioxide, aluminium oxide, titanium dioxide, aluminium hydroxide, nitrides (e.g. silicon nitride), kaolin, talc, wollastonite, feldspar, mica, starch, starch derivatives, cellulose, cellulose derivatives, zinc glass, boron silicate glass, polycarbonates, polyepoxides, polyethylene and all materials which have already been mentioned in the reactive systems and which fulfil the conditions stated above.

[0079] As fibres, it is preferred to use polymer fibres, ceramic fibres, natural fibres, carbon fibres and glass fibres. Examples comprise fibres made of cellulose, cellulose derivatives, wood, polypropylene, aramide, silicon carbide, aluminium silicate and from all materials which have already been named in the reactive systems and which fulfil the conditions stated above.

[0080] Typical particle sizes for fillers and fibres lie between 20 and 150 μm . If the fibres or fillers are also coated as described above, their primary particle size can also be < 1 μm .

[0081] In addition to the unimodal grain size distribution, the fillers can also reveal a polymodal (e.g. bimodal, trimodal) grain size distribution. It is preferred to choose the distribution so that the powder particles achieve as high as possible a packing density.

Flexibilisers

[0082] In order to be able to increase the flexibility of the components, small quantities of water-soluble polymers may be added to the system as flexibilisers. In order to obtain water-resistant 3D objects, the quantity of water-soluble polymers must not be too large. The mechanical strength of the 3D objects, however, is not determined primarily by the flexibilisers but mainly by the chemical reactive system. Typical average particle sizes of the flexibilisers lie between 10 and 100 μm .

[0083] Suitable polymers are e.g. polyvinyl alcohol, polyvinyl pyrrolidone (and its copolymers), gelatine and pregelinated starch.

Special reactive system

[0084] Radically polymerisable components may also be added to the system as a special reactive system, which have one or more ethylenically unsaturated groups. Such systems are already widely known in combination with ionomer cements in the dental branch and are described, for example, in the US patent specifications 5,154,762 and 6,136,885.

[0085] The radically polymerisable components are preferably water-soluble and can be contained in the powder and/or the ink.

[0086] This may involve monomers, oligomers, prepolymers or polymers.

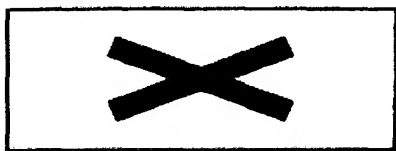
[0087] Preferably, it is a matter of water-soluble mono-, di- and polymethacrylates with a low viscosity in water such as 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, polyethylene glycol monomethacrylates (e.g. molecular weight = 400), ethylene glycol methacrylate, glycerine monomethacrylate, methyl methacrylate, 2-tert-butylaminomethyl methacrylate, tetrahydrofurfuryl methacrylate, ethyltriglycol monomethacrylate, dimethylaminoethyl methacrylate, methacrylic acid, polyethylene glycol dimethacrylates (e.g. molecular weight = 400), glycerine dimethacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, urethane methacrylate, bis-EMA (ethoxylated bisphenol-A-dimethacrylate) as well as polymethacrylates (homo- and copolymers) of the stated mono- and dimethacrylates. Mono- and dimethacrylates are particularly preferred.

[0088] Preferably, metal salts of methacrylate and acrylate are involved, such as sodium methacrylate, potassium methacrylate, ammonium methacrylate, magnesium methacrylate, calcium methacrylate, aluminium methacrylate, zinc methacrylate, zirconium methacrylate, zirconium trihydroxymonomethacrylate, zirconium dihydroxydimethacrylate, sodium acrylate, potassium acrylate, ammonium acrylate, magnesium acrylate, calcium acrylate, aluminium acrylate, zinc acrylate, zirconium acrylate, zirconium trihydroxymonoacrylate, zirconium dihydroxyacrylate.

[0089] Components may also be used by preference which contain ethylenically unsaturated groups and acid groups (e.g. $-\text{COOH}$) or ethylenically unsaturated groups, acid groups (e.g. $-\text{COOH}$) and base groups (e.g. $-\text{NH}_2$) in one component. These include the acid esters which can be formed from the above-stated mono- and dimethacrylates with the polyacids stated in reactive system 1 or the copolymers from polyacid and polybase.

[0090] In particular, systems which are described as so-called "photocurable ionomers" in the US patent specification 5,925,715 (column 3, line 31 to column 7, line 10) are involved. These "photocurable ionomers" have sufficient ionic groups (e.g. $-\text{COOH}$) which in the presence of water can bring about a reaction with the inorganic reactive component from reactive systems 3 and 4 (e.g. zinc oxide) with the polycation from reactive systems 2 and 6 (e.g. polyvinylpyridine hydrochloride) or the polybase from reactive systems 1 and 5 (e.g. polyvinyl pyridine), and also sufficiently ethylenically unsaturated groups in order to be able to bring about a polymerisation initiated by a redox system.

[0091] By preference, ethylenically unsaturated phosphoric acid esters and their salts may also be used as described, for example, in US patent specifications 4,499,254, 4,222,780, 4,235, 633, 4,259,117, 4,368,043 and 4,514, 342. It is particularly preferred if it is a question of ethylenically unsaturated methacrylate monophosphate of the formula:



in which R is a hydrocarbon group with 2-40 carbon atoms with a valency of $n+1$. R may be interrupted by one or more oxygen atoms, if necessary substituted with halogen atoms, hydroxyl or amino groups and comprise an aliphatic group, a cycloaliphatic group or an aryl group. n is a whole number with at least value 1, preferably 1 or 2.

[0092] In particular, it is, for example, hydroxyethyl methacrylate monophosphate, glycerine dimethacrylate phosphate, hydroxypropyl methacrylate monophosphate, ethylene glycol monomethacrylate monophosphate and triethylene glycol monomethacrylate monophosphate.

[0093] The preferred quantity of the ethylenically unsaturated component amounts is between 0.1 and 50 % by weight (referred to the weight of the powder) and more preferably between 0.2 and 20 % by weight. If the ethylenically unsaturated component of the ink is added, the dynamic viscosity of the ink should not exceed 50 mPa · s as otherwise, blockage of the jets can occur. A dynamic viscosity of < 25-30 mPa · s is preferred.

[0094] In order to initiate the polymerisation of the radically polymerisable components, a redox catalyst system is added. Various suitable redox systems are described in US patent specifications 5, 154,762 and 6,136,885.

[0095] The oxidising agent should react with the reducing agent or otherwise act with it so that free radicals are generated which are able to initiate the polymerisation of the ethylenically unsaturated component. The oxidising agent and the reducing agent are preferably both sufficiently stable in storage. They should be sufficiently water-soluble so that they are distributed quickly in the powder by rapid dissolution and facilitate a radical reaction rate. Useful oxidising agent/reducing agent pairs are indicated in G.S. Misra and U.D.N. Bajpai, "Redox Polymerization", Prog. Polym. Sci., 8, 61-131 (1982).

[0096] Preferred reducing agents comprise amines (in particular aromatic amines), ascorbic acid cobalt(II) chloride, iron chloride, iron sulphate, hydrazine, hydroxyamine, oxalic acid, thiourea and dithionite, thiosulphate, benzol sulphinate or sulphite salts.

[0097] Preferred oxidising agents include persulphates such as sodium, ammonium and alkylammonium persulphate, benzoyl peroxide, hydroperoxides such as tert-butyl-hydroperoxide and cumene hydroperoxide, cobalt(III) salts like cobalt(II) chloride, iron(III) salts like iron(III) chloride, perboric acid and its salts, permanganate salts, hydrogen peroxide and combinations thereof.

[0098] The reducing agents and oxidising agents can be present in the ink and/or the powder. However, reducing agents and oxidising agents must not be located together with the ethylenically unsaturated component. A common combination of these three components in the powder is preferably also to be avoided.

[0099] The preferred quantity for each reducing agent and oxidising agent is between 0.01 and 10 % by weight, more preferably between 0.02 and 5 % by weight referred to the ethylenically unsaturated component.

[0100] In order to prevent premature polymerisation of the ethylenically unsaturated component before the printing process, the powder or the ink may still contain (according to where the ethylenically unsaturated component is situated) inhibitors such as benzophenone, hydroquinone or hydroquinone monomethyl ether.

Process aids

[0101] Components may also be added to the reactive system which improve the layer application of the reactive system by increasing the flowability thereof. These include, for example, aerosil and spray-dried PVA.

Ink

[0102] Solvents such as water, ketones, alcohols, esters and their mixture may be used as ink, water and water-based solvents being preferred. Examples of suitable ketones are acetone and methylethylketone. As alcohols, methanol, ethanol and isopropanol may be used, for example. Examples of suitable esters are ethyl acetate and acetoacetic ester. The ink may, if necessary, also contain additives like flow rate accelerators and humectants which already contain the above-mentioned reaction retarders as well as surfactants.

[0103] Suitable flow rate accelerators are, for example, ethylene glycol diacetate, potassium aluminium sulphate, isopropanol, ethylene glycol monobutyl ether, diethylene monobutyl ether, dodecyldimethylammonium propionate sulphate, glycerine triacetate, ethyl acetoacetate, polyvinyl pyrrolidone, polyethylene glycol, polyacrylic acid or sodium polyacrylate.

[0104] As a surfactant, sodium dodecyl sulphate (SDS), for example, is suitable.

[0105] Suitable humectants are, for example, glycerine, ethylene glycol or propylene glycol.

[0106] The examples indicated below explain the invention and are not to be seen as restrictive.

[0107] The indicated examples 1 and give reproduce preferred embodiments of the reactive system 3 according to the invention. Reactive system 3 consists of reactants 1 and 2 and a reaction retarder. Reactant 1 is the inorganic reactive component and reactant 2 the polyacid component of reactive system 3. The comparison examples 1 and 2 show known powder systems which have been used to date for 3D printing processes.

[0108] The reactive systems consist in each case of a reactive system powder and the pertinent ink and are processed in a way well known per se by means of an inkjet 3D printing process (cf. US patent specifications 5,204,055 and 5,902,441) into a water-resistant 3D object with improved strength. Devices which are suitable for the inkjet 3D printing process of the present invention are, for example, e.g. devices of the type ZTM400 and ZTM406 of the firm Zcorporation, 20th North Avenue, Burlington, MA01803, USA as well as their successor models. In addition, devices of the type Desk ModelerTM of the firm Buss Modeling Technology GmbH (bmt), Florinstraße 18, D-56218 Mülheim-Kärlich, Germany are suitable. The proportion of the solvent/swelling agent, which is sprayed by the ink jet print head, in relation to the powder, is limited by the technology. Suitable ratios of solvent/swelling agent to powder amount of preferably 5-50 % and in particular 10-30 %.

[0109] The 3D objects obtained can be subjected to other post-treatments such as cleaning, heat treatment, infiltration, sanding and coating. Heat treatment and infiltration (wax, resin infiltration, infiltration with aqueous or organic solutions of inorganic salts, organic or polymer compounds) increase the mechanical strength of the object. Infiltration also reduces the porosity.

Example 1

Powder

Component material	Material used	Composition (% by weight)	average particle size (μm)
Reactant 1	Calcium aluminium silicate glass (baseline dentsply K900412)	84.64	d50 = 57
Reactant 2	Polyacrylic acid $M_w = 15000\text{--}25000$ g/mol	14.5	d50 = 40-45
Reaction retarder	Tartaric acid	0.86	d50 = 10

Ink

Component material	Material used	Composition
Solvent	water	85 % by weight
Flow rate accelerator	isopropanol	10 % by weight
Humectant	Glycerine	5 % by weight
Surfactant	SDS	2 g/100 ml
Reaction retarder	Tartaric acid	10 g/100 ml

Example 2

Powder

Component material	Material used	Composition (% by weight)	average particle size (μm)
Reactant 1	Zinc oxide/magnesium oxide (Poly F Plus Base - Dentsply K900222)	94	d50 = 63
Reactant 2	Polyacrylic acid $M_w = 15000\text{--}25000$ g/mol	6	d50 = 40-45

Ink

Component material	Material used	Composition (% by weight)
Solvent	water	85
Flow rate accelerator	isopropanol	10
Humectant	glycerine	5
Surfactant	SDS	1 g/100 ml

Comparison example 1

Powder:

ZP 14 (powder based on starch-cellulose-dextrose of the firm Zcorporation).

Ink:

ZB4a (Ink based on water of firm Zcorporation).

Comparison example 2

Powder:

Polyvinyl alcohol (power of the firm bmt for the DeskModeler™).

Ink:

Ink based on water of firm bmt.

[0110] From the systems of examples 1 and 2, test specimens were produced on the Deskmodeler of the firm bmt. From the systems of the comparison examples 1 and 2, comparison test specimens were produced either on a 3D printer of the type Z402 of the firm Zcorporation (ZP14) (comparison example 1) or on the Deskmodeler of the firm bmt (comparison example 2).

Bending strength measurement - 3-point bending test

[0111] The bending tests were carried out on the material test machine Z005/TN2A of the firm Zwick. The measurement took placed using a 5 kN load sensor; the radius of the bending punch was 5 mm and the radius of the bending support 2 mm.

[0112] The span was 50 mm, the height of the test specimens 7.5 mm and the width of the test specimens 10 mm. The preliminary force was 1 N, the preliminary force rate 10 mm/in and the test rate 5 mm/min. The measurement results were evaluated with the software testXpert V 7.01 and are indicated in Table 8.

Table 8

Material of the test specimen	Bending strength	E-modulus
	(Mpa)	(Mpa)
Calcium aluminium silicate glass + Polyacrylic acid (Example 1)	3.2 ± 0.11	890 ± 60
Zinc oxide/magnesium oxide (Example 2)	5.1 ± 0.17	1800 ± 50
ZP 14 (comparison example 1)	2.6 ± 0.11	330 ± 25
Polyvinyl alcohol (Comparison example 2)	1.1 ± 0.1	59 ± 7.3

[0113] It can be seen from Table 8 that the test specimens produced according to examples 1 and 2 compared to the test specimens produced according to the comparison examples 1 and 2 reveal superior bending strength and E-modulus values.

[0114] In addition, it can be seen from Fig. 1 that the test specimen according to example 1 of the reactive system according to the invention without post-treatment is distinguished by improved water resistance compared to the systems known to date.

[0115] Thus, one can see in Illustration 2 of Fig. 1 that test specimens which are created with the material from comparison example 1 (ZP 14, starch-cellulose-powder), dissolve almost completely after only a few minutes into their powder constituents if they are exposed to an aqueous environment.

[0116] Test specimens which are created according to comparison example 2 (polyvinyl alcohol) dissolve only gradually in an environment of water. However, these test specimens begin to swell after only a few minutes in water, which leads to softening of the test specimen (cf. illustrations (4) and (5) of Fig. 1).

[0117] 3D test specimens which have been created according to example 1 are distinguished by water resistance. Even after 24 hours in water (cf. illustration (7) of Fig. 1) the test specimens retain their shape and do not dissolve into their powder constituents. In addition, they undergo no softening as is the case with the test specimens according to the comparison examples 1 (ZP 14) and 2 (polyvinyl alcohol) (cf. illustrations (7) and (8) of Fig. 1).

Patent Claims

1. Reactive system for 3D printing comprising at least one first component and at least one second component, the first and the second components reacting chemically with one another after adding a liquid medium and forming a solid.
2. Reactive system according to Claim 1, characterised in that the first component is a polyacid and the second component a polybase.
3. Reactive system according to Claim 1, characterised in that the first component is a polyanion and the second component a polycation.
4. Reactive system according to Claim 1, characterised in that the first component is a polyacid and the second component an inorganic reactive component.
5. Reactive system according to Claim 1, characterised in that the first component is a polyanion and the second component an inorganic reactive component.
6. Reactive system according to Claim 1, characterised in that the first component is a polybase and the second component an inorganic reactive component.
7. Reactive system according to Claim 1, characterised in that the first component is a polycation and the second component an inorganic reactive component.
8. Reactive component according to Claim 4 or 5, the inorganic reactive component being selected from the group consisting of barium oxide, calcium oxide, magnesium oxide, zinc oxide, zinc oxide/magnesium oxide, aluminium chloride, aluminium stearate, aluminium sulphate, aluminium acetate, calcium carbonate, calcium ascorbate, calcium lactate, calcium saccharate, calcium hydrogen phosphate, calcium chloride, calcium hydroxide, calcium phosphate, calcium acetate, hydroxylapatite, calcium nitrate, calcium fluoroborate, zinc chloride, zinc stearate, zinc acetate, zinc gluconate, zinc sulphate, barium nitrate, strontium nitrate, borate glasses, phosphate glasses, fluoroaluminium silicate glasses, calcium aluminium silicate glasses as well as mixtures thereof.

9. Reactive system according to Claim 6 or 7, the inorganic reactive component consisting of slightly hygroscopic phosphates, hydrogen phosphates, diphosphates, triphosphates, sulphates, sulphites, disulphates, thiosulphates, tetraborates and their water-soluble sodium, potassium and ammonium salts.
10. Reactive system according to Claim 2 or 4, the polyacid being selected from the group consisting of alginic acid, gum arabic, nucleic acids, pectins, proteins, carboxymethyl cellulose, ligninsulphonic acids, acid-modified starch, polymethacrylic acid, polymethacrylic acid copolymer with methyl methacrylate, polyvinyl sulphonic acid, polystyrene sulphonic acid, polysulphuric acid, polyvinyl phosphonic acid, polyvinyl phosphoric acid, acrylic acid, itaconic acid, mesaconic acid, citraconic acid, aconitic acid, maleic acid, fumaric acid, glutaconic acid, tiglic acid and methacrylic acid and the copolymers of these polyacids with acrylamide, acrylic nitrile, acrylic acid esters, vinyl chloride, allyl chloride, vinyl acetate and 2-hydroxyethyl methacrylate.
11. Reactive system according to one of Claims 2, 6, 9 and 10, the polybase being selected from the group consisting of chitosan, polyethylenimine, polyvinyl amine, polyvinyl pyridine, polydiallyl dimethylamine, poly[2-(N,N-dimethylamine)-ethyl acrylate], poly[4-(N,N-dimethylamine)-methylstyrene] and the copolymers of these polybases with acrylamide, acrylic nitrile and acrylic acid esters.
12. Reactive system according to one of Claims 3, 5 and 8, the polyanion being selected from the sodium, ammonium or potassium salts of alginic acid, gum arabic, nucleic acids, pectins, proteins, carboxymethyl cellulose, ligninsulphonic acids, acid-modified starch, polymethacrylic acid, polymethacrylic acid copolymer with methyl methacrylate, polyvinyl sulphonic acid, polystyrene sulphonic acid, polysulphuric acid, polyvinyl phosphonic acid, polyvinyl phosphoric acid, acrylic acid, itaconic acid, mesaconic acid, citraconic acid, aconitic acid, maleic acid, fumaric acid, glutaconic acid, tiglic acid and methacrylic acid and the copolymers of these acids with acrylamide, acrylic nitrile, acrylic acid esters, vinyl chloride, allyl chloride, vinyl acetate and 2-hydroxyethyl methacrylate.
13. Reactive system according to one of Claims 3, 7, 8 and 12, the polycation being selected from the ammonium compounds or quaternary ammonium compounds of chitosan, polyethylenimine, polyvinyl amine, polyvinyl pyridine, polydiallyl dimethylamine, poly[2-(N,N-dimethylamine)-ethyl acrylate], poly[4-(N,N-dimethylamine)-methylstyrene] and the copolymers of these polybases with acrylamide, acrylic nitrile and acrylic acid esters.
14. Reactive system according to one of Claims 2 to 13, the average molecular weights of the polyacids/polyanions and the polybases/polycations lie between 500 and about 1,000,000 g/mol, preferably between 5000 and about 250,000 g/mol and in particular between 5000 and about 100,000 g/mol.
15. Reactive system according to one of Claims 4 to 14, the particle size of the inorganic reactive component lying below 300 μm .
16. Reactive system according to one of Claims 2 to 15, the particle size of the polybase/polycation and of the polyacid/polyanion lying below 300 μm .
17. Reactive system according to one of Claims 1 to 16, also comprising one or more additive(s) selected from the group consisting of reaction retarders, fillers, flexibilisers, process aids and special reaction systems.
18. Reactive system according to Claim 17, the reaction retarders being selected from the group consisting of salicylic acid, tartaric acid, dihydroxytartaric acid, oxalic acid, citronic acid, ethylene diaminetetraacetic acid (EDTA) and their sodium and potassium salts, sodium phosphate, sodium hydrogen phosphate, sodium dihydrogen phosphate, magnesium oxide and tin fluoride.
19. Reactive system according to Claim 17 or 18, the fillers being selected from the group consisting of sand, quartz, silicon dioxide, aluminium oxide, titanium dioxide, aluminium hydroxide, nitrides, kaolin, talc, wollastonite, feldspar, mica, starch, starch derivatives, cellulose, cellulose derivatives, zinc glass, boron silicate glass, polycarbonates, polyepoxides, polyethylene, carbon fibres, glass fibres, fibres made of cellulose, cellulose derivatives, wood, polypropylene, aramide, silicon carbide and aluminium silicate.
20. Reaction system according to one of Claims 17 to 19, the flexibilisers being selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone and copolymers thereof, gelatine and pregelatinated starch.
21. Reactive system according to Claim 17 or 18, the fillers being selected from the group consisting of aerosil and spray-dried PVA.
22. Reactive system according to one of Claims 17 to 21, the special reactive systems consisting of radically polymerisable components with one or more ethylenically unsaturated groups or of radically polymerisable components with one or more ethylenically unsaturated groups and acid and base groups.
23. Reactive system according to one of Claims 1 to 22, the liquid medium being water, an aqueous-organic solvent or an organic solvent miscible with water of a mixture thereof.
24. Reactive system according to Claim 23, the liquid medium being selected from the group consisting of acetone, methylethylketone, methanol, ethanol, isopropanol, ethyl acetate, acetoacetic ester and their mixtures with each other and with water.
25. Reactive system according to one of Claims 1 to 24, the formed solid being water-resistant.

- Empty page -

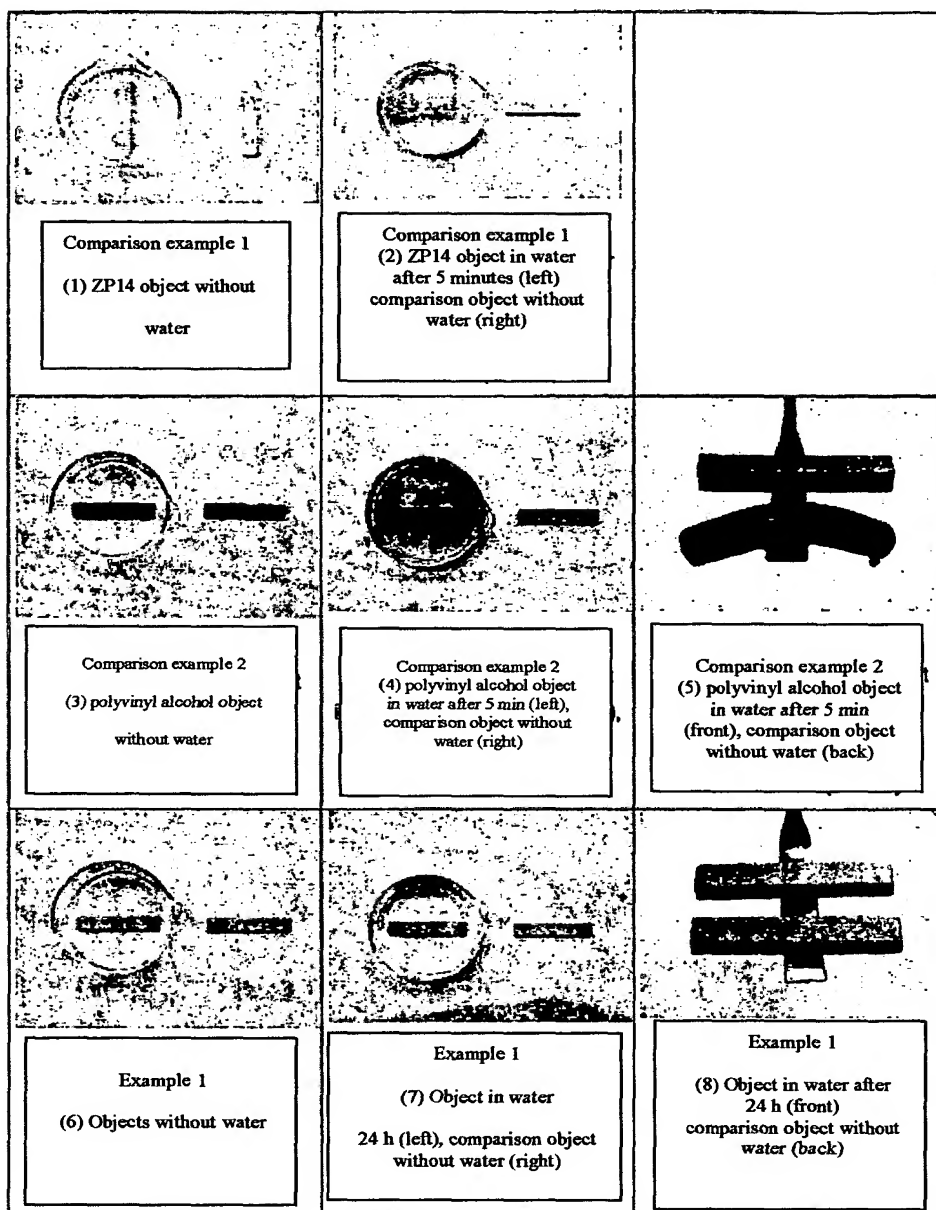


Fig. 1